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Scots pine resin and BVOC emissions in relation to tree water dynamics

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Trees have various mechanisms for avoiding and mitigating biotic and abiotic stresses. Resin is one such mechanism, and it is essential for conifer trees. Conifer resin is also a large pool of monoterpenes that – similarly to other biogenic volatile organic compounds (BVOCs) produced by plants, e.g. methanol, acetone and acetaldehyde – play important roles in tree signalling and atmospheric chemistry once emitted to ambient air. BVOC emissions from various tree parts and resin dynamics depend on environmental variables, with intrinsic effects on conifer defence.

This thesis aims to clarify the environmental and physiological drivers of resin dynamics and BVOC emissions from the shoots and stem of mature boreal Scots pines (*Pinus sylvestris*) in field conditions, with special attention given to the effect of tree water relations. Resin pressure dynamics were studied using pressure transducers and BVOC emissions using an online mass spectrometer and dynamic chamber system. Resin and monoterpene emission compositions were analysed based on gas chromatography measurements.

Temperature explained resin pressures and BVOC emissions from both the shoots and stems of Scots pine in the short term. Over a longer period, resin pressures and stem monoterpene emissions decreased with decreasing soil water availability and water potential in stem. In addition, the emission dynamics of water-soluble acetaldehyde, methanol, and acetone from the shoots and stem were connected to transpiration rate and soil water content, indicating an important effect of their transport in the xylem sap.

These results show that although often overlooked, tree stems are an important source of BVOCs and that even relatively small changes in water availability may alter BVOC and resin dynamics despite their strong short-term temperature control. This information may help to understand the potential susceptibility of conifer trees to biotic stresses in various environmental conditions and improve BVOC emission modelling by accounting for stem emission dynamics.

Keywords: resin, monoterpene, methanol, acetaldehyde, acetone, Scots pine

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LIST OF ORIGINAL ARTICLES

The thesis includes the following publications, hereafter referred to with their Roman numerals.

I. Rissanen, K., Hölttä, T., Vanhatalo, A., Aalto, J., Nikinmaa, E., Rita, H. & Bäck, J. (2016). Diurnal patterns in Scots pine stem oleoresin pressure in a boreal forest. *Plant, Cell and Environment* 39: 527–538. doi: 10.1111/pce.12637

II. Rissanen, K., Hölttä, T., Barreira, L.F.M., Hyytinen, N., Kurtén, T. & Bäck, J. (2019). Temporal and spatial variation in Scots pine resin pressure and composition. *Frontiers in Forests and Global Change* 2: 23. doi: 10.3389/ffgc.2019.00023

III. Rissanen, K., Vanhatalo, A., Salmon, Y., Bäck, J. & Hölttä, T. (2019). Stem emissions of monoterpenes, acetaldehyde and methanol from Scots pine affected by soil and tree water status. Manuscript.

IV. Rissanen, K., Hölttä, T. & Bäck, J. (2018). Transpiration directly regulated the emissions of water-soluble short-chained OVOCs. *Plant, Cell and Environment* 41: 2288–2298. doi: 10.1111/pce.13318

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1 INTRODUCTION

Trees stand still, living for tens, hundreds, or even thousands of years without moving from where they landed as seeds. Where they stand, they must find all they need to sustain themselves and where they stand, they must resist all types of weather and invasions from other organisms. Nevertheless, trees are among the most long-living individual organisms on our planet.

To survive and outlive the challenges in their habitat, trees have developed a multitude of mechanisms and processes to acquire water and nutrients, transport substrates where they are needed and defend themselves against herbivores and pathogens. The functioning and fine-tuning of these processes have been – and still are – a great puzzle for researchers.

Conifer trees, one of the most abundant groups of plants, have developed one such successful survival mechanism. To deter herbivores and pathogens, conifers produce resin. Resin is a viscous liquid that flows and covers wounds on the tree surfaces, and it is toxic for many small organisms. It is also a large pool of monoterpenes, i.e. volatile molecules that create the distinct odour of resin and the odour of forest. While we detect these scents as a pleasant addition to the scent scape, many organisms including plants and insects use them to receive information from their surroundings. They alert for possible hosts, prey or stress.

Alongside monoterpenes, trees produce a whole spectrum of various volatile compounds, the functions of which are not thoroughly understood at the tree level or in the ecosystem. However, these compounds are known to play an important role in atmospheric chemistry, affecting air quality and cloud formation, for example. Thus, instead of just surviving in their environment, trees actively affect the processes surrounding them.

Despite their fine mechanisms and despite resin, conifers currently face new challenges, including rapid shifts in their environment caused by land-use changes and global warming with its side effects. Thus, understanding the mechanisms of tree survival and their interactions with other organisms and the atmosphere is increasingly important.

1.1 Resin

Resin, or oleoresin, is a sticky, gold-coloured liquid from conifer trees that embodies the odour of forest and freshly sawn wood. It has long been a valued raw material: fresh resin has been used to heal wounds and hardened resin chewed to clean teeth, but most importantly, resin has made its mark in history on the sides of sailing ships – pitch and tar used to coat ships are products from slow-burning wood, high in resinous compounds. Nowadays, pine resin is used in the production of chemicals for various industrial and household uses, e.g. in adhesives, coatings, fragrances, and flavours (Coppen and Hone 1995; Langenheim 2003). However, more important to humans, resin is important for trees. It is an essential part of the first-line of defence of conifer trees against herbivores and pathogens.

1.1.1 Resin composition and storage structures

Resin is found in most conifer species. For example, nearly all genera of the Pinaceae family, which is the largest conifer family, can produce resin. Resin composition has been studied since the 1930s and increasingly since the 1960s (e.g. Kurth and Sherrard 1931; Smith 1964a b c), with varying intensities until the present. During this time, the methods for resin component extraction and identification have developed considerably, allowing increasingly reliable and comprehensive results on resin composition.

Resin contains approximately 75% of resin acids that are non-volatile diterpene acids and 25% of volatile monoterpenes along with small quantities of volatile sesquiterpenes (Croteau and Johnson 1985). Sometimes other wood extractives, such as phenolic compounds, are also classified as resins, but in the following, resin only includes terpene compounds. The mixture of the two terpene types enables resin functions: volatile terpenes act as solvents that mobilise non-volatile terpenes, whereas non-volatile terpenes increase resin viscosity and cause its crystallisation. The most common diterpenes in *Pinus* species are abietane- and pimarane-type diterpenic acids, such as abietic and pimaric acids (Langenheim 2003), and the most common monoterpenes are α-pinene, ß-pinene, Δ^3-carene, sabinene, myrcene, limonene and ß-phellandrene (Smith 2000) (Figure 1).

However, resin composition, and its monoterpene concentrations in particular, vary considerably between species, populations and even individuals of the same species (Smith 1964a; Zavarin and Cobb 1970; Marpeau et al. 1989; Latta et al. 2000, 2003; Fäldt et al. 2001; Thoss et al. 2007; Kännaste et al. 2013), and the composition seems to be under genetic control (Hanover 1966, 1992). Resin composition may also vary between different tissues within a single tree, especially when comparing the needles, phloem and sapwood (Latta et al. 2000). However, resin composition is quite uniform within the sapwood (Smith 1964c). Despite the variation within and between trees, the temporal variation of resin composition should be limited in the absence of stresses: because resin production is small in comparison to resin pool size, the turnover is long, up to several years (Wilson et al. 1963; Gershenzon et al. 1993).

The structures for resin storage differ between species: resin can be stored in isolated resin cells scattered in the stem (e.g. in *Thuja*), in resin blisters or glands that are round multicellular structures in the sapwood and bark (e.g. in *Abies* and *Sequoia*) or within resin ducts that are long, intercellular cavities in the sapwood, bark, roots, needles and buds (e.g. in *Pinus*, *Picea* and *Larix*). The resin duct system in pines (*Pinus*) is considered highly developed, forming a dense network of partially interconnected longitudinal and radial canals within the stem (Figure 2) (Werker and Fahn 1969; Bosshard and Hug 1980; Phillips and Croteau 1999; Zhang et al. 2008). Pine and spruce (*Picea*) resin ducts are enveloped by one or several layers of thin-walled epithelial cells that produce resin acids and monoterpenes in their plastids and sesquiterpenes in their endoplasmic reticulum (Dell and McComb 1979; Langenheim 2003; Zulak and Bohlmann 2010). The epithelial cells are surrounded by layers of thick-walled sheath cells (Wu and Hu 1997). Epithelial cells can remain biologically active for several years in pines, whereas the sheath cells can be dead (Wu and Hu 1997).

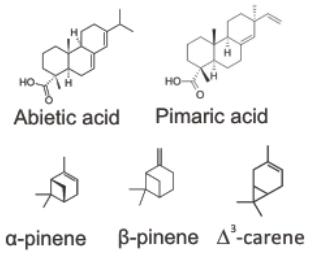

Figure 1. Crystallising resin and the most common components of resin in *Pinus* species (photo by Kaisa Rissanen).

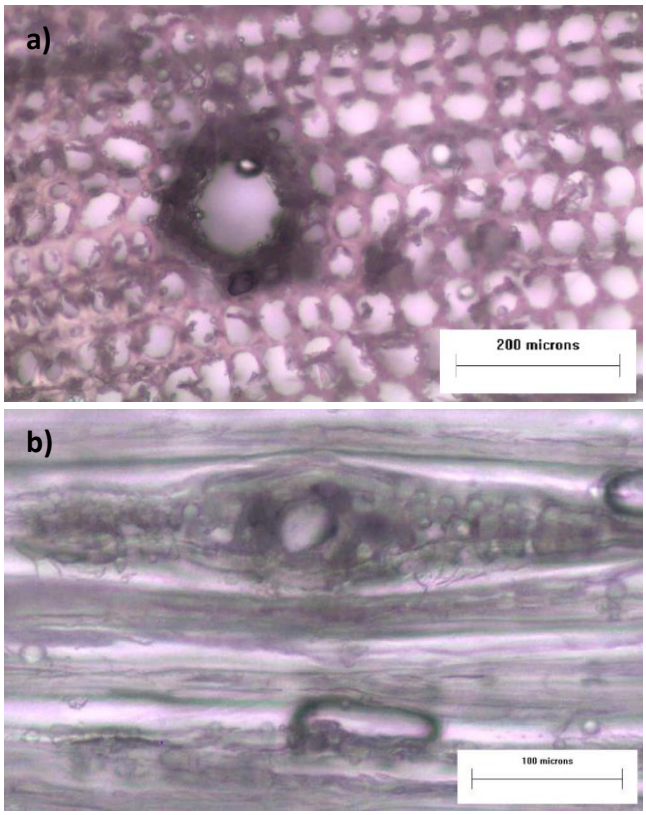

Figure 2. a) Axial (vertical) resin duct and b) smaller horizontal resin duct in a ray of Scots pine (*Pinus sylvestris*) (photo: Study I, Rissanen et al. 2016).

1.1.2 Resin in conifer defence

Resin has been an important subject of research because of its commercial value, but even more because of its central role in the defence of conifer trees. For example, during and after the outbreaks of southern pine beetle (*Dendroctonus frontalis*) in southern USA in the 1970s, researchers concentrated on identifying the traits that made local pine species and individual trees either susceptible or resistant to the bark beetle infestations. These traits included resin composition and flow, and the density of resin ducts, for example.

Resin protects the tree both mechanically and chemically against pathogens and pest insects, for example, herbivorous larvae and bark beetles. As a mechanical defence, resin pitches out intruders and seals wounds. In pines, resin in resin ducts is stored under a pressure that can exceed 10 bar (Bourdeau and Schopmeyer 1958; Vité 1961; Vité and Wood 1961), which enables a rapid release of resin after the duct has been injured. The flow of resin released from the wound can overwhelm and drown an invasive insect. After resin flushes to the wounded site, the resin monoterpenes evaporate, and the resin acids crystallise to form a seal that protects the wound from further intruders (Figure 3). The chemical defence comprises resin compounds that are either harmful for herbivores or pest insects, such as monoterpenes limonene, Δ^3-carene, and α- and β-pinene (Smith 1965, 1966; Phillips and Croteau 1999; Seybold et al. 2006; Reid et al. 2017), anti-fungal, such as resin acids abietic acid and isopimaric acid (Kopper et al. 2005) or anti-bacterial, such as monoterpenes thymol, carvacol, p-cymene and y-terpinene (Cristani et al. 2007). These compounds may affect

herbivore preferences, larvae development (Langenheim 1994) and fungal germination or growth (Kopper et al. 2005), but they can also be used as signals by host-seeking insects (Phillips and Croteau 1999) or their predators and parasites (Langenheim 1994). In addition, monoterpenes may transmit signals within plants and between plant individuals (Baldwin et al. 2006): high concentrations of stress-related monoterpenes in the air may provoke the production of defensive compounds and prepare other plant parts or even other plants against potential herbivory (Baldwin et al. 2006).

However, even from the insect perspective, resin is not only harmful. Certain insects can tolerate high concentrations of resin acids and monoterpenes, and find protection within resinous tissues (Langenheim 1994). European sawfly larvae (*Neodiprion certifer*) can even store resin acids for their own defence and eject them onto predators (Eisner et al. 1974). In addition, wood ants carry resin into their nests to protect it against pathogens (Chapuisat et al. 2007; Castella et al. 2008).

1.1.3 Resin dynamics

While studying the susceptibility and resistance of certain pines to a mass attack of bark beetles, researchers found that not only do resin composition and certain toxic compounds play a central role in the resistance, but so also do the production, flow and pressure of resin. Although none of these variables explained tree resistance alone (Lorio 1994), trees more resistant to bark beetles were observed to have large and persistent resin flows (Smith 1966; Hodges et al. 1979; Strom et al. 2002) and high resin pressure (Vité and Wood 1961; Wood 1962) among other factors.

Resin pressure is not a static feature of a tree, but rather it changes depending on water availability and tree water relations at different time scales. At a seasonal scale, decreasing water availability causes a decreasing trend in resin pressure, partly explaining the susceptibility of trees to bark beetles in dry conditions (Vité 1961; Barret and Bengtson 1964; Lorio and Hodges 1968a). At a daily scale, high resin pressures have been invariably measured at night when the water potential in stem is high and low resin pressures have been observed in the daytime when the water potential is low (Schopmeyer et al. 1954; Bourdeau and Schopmeyer 1958; Vité 1961; Hodges and Lorio 1968, 1971; Lorio and Hodges 1968b; Helseth and Brown 1970; Neher 1993). These dynamics have been explained by changing xylem water tensions and turgor pressures within the stem. On the one hand, high transpiration in the daytime decreases the water potential in the xylem, which shrinks the xylem tracheids and creates more space for the intercellular resin ducts, decreasing the resin pressure (Helseth and Brown 1970; Neher 1993). On the other hand, low water potential also draws water from the epithelial cells lining the resin ducts, decreasing their turgor pressure and thus the pressure they pose on the resin (Vité 1961).

The large body of knowledge concerning pine resin dynamics has been collected in the drought-prone pine forests of southern USA, but similar understanding is lacking in the cool and moist boreal environment. The role of resin-base defence is crucial in boreal forests as bark beetles pose a major threat to conifer trees particularly after storms and during and after dry years (see Bakke, 1983). Storms and windfalls along with droughts or inundations may become more frequent because of climate change, favouring bark beetle epidemics. In addition, warmer and longer growing seasons in the north may allow bark beetles to produce two broods in one growing season, which also increases the risk of epidemics (Schlyter et al. 2006). Thus, understanding the factors affecting tree defence also in the boreal environment is important for predicting and preventing forest dieback.

Figure 3. Resin leaked from an Aleppo pine (*Pinus halepensis*) stem where bark beetles have entered the stem (photo by Kaisa Rissanen).

1.2 Volatile organic compounds (VOCs)

Monoterpenes and sesquiterpenes, i.e. the volatile constituents of resin, belong to a group of compounds called volatile organic compounds (VOCs) and more specifically to biogenic volatile organic compounds (BVOCs). They are a variety of hydrocarbon molecules produced and emitted by plants as a part of their secondary metabolism, meaning that these compounds are not directly necessary for normal growth and reproduction. However, they serve many purposes, such as resistance against heat and high irradiation along with signalling and defending against biotic stresses, but they may also leak out as side products of other metabolic processes in plants. BVOCs have been of growing interest both because of new findings on the signalling occurring within and between plants or between plants and insects and because of their important role in atmospheric chemistry.

Once emitted into the ambient air, BVOCs react with atmospheric oxidants: hydroxyl radical (OH), ozone (O_3) and nitrate radicals (NO_3) (Atkinson and Arey 2003). These reactions have various consequences in atmospheric chemistry. First, BVOCs reacting with OH reduce the atmospheric sink for methane, meaning that high BVOC concentrations lengthen the lifetime of methane (Kaplan et al. 2006). Second, BVOCs react with nitrogen oxides (NO_x) originating from anthropogenic sources, such as industry and transport, and produce O_3. Thus, high BVOC concentrations combined with high NO_x concentrations increase the tropospheric O_3 concentration, contributing to the poor air quality in already polluted areas (Atkinson 2000). In contrast, BVOCs remove O_3 in areas with low NO_x concentrations, contributing to good air quality (Atkinson and Arey 2003). Third, BVOCs participate in processes that impact the regional and global radiative budgets. BVOC oxidation products initiate or participate in the growth of secondary organic aerosols (SOAs) (Ziemann and Atkinson 2012). When large enough, SOAs form cloud condensation nuclei

that evolve into cloud droplets and form clouds, the properties of which depend on the quantity and size of the cloud droplets (Andreae and Rosenfeld 2008; Kazil 2010; Rosenfeld 2014). Together with SOAs, clouds increase the albedo and scatter solar radiation, thus they have a net cooling effect on the climate (Kulmala et al. 2013; Paasonen et al. 2013; Kulmala 2014). Radiation scattering also increases the ratio of diffuse to direct radiation that is advantageous for plant growth (Gu 2002) and further for the BVOC emissions, creating a cooling feedback loop (Kulmala et al. 2013).

The reactions of BVOCs in the atmosphere are important parts of climate modelling, and detailed information on BVOC emissions budgets from the vegetation is necessary to accurately represent the BVOC effects. The remaining questions concerning the role of BVOCs include, for example, the contributions of various ecosystem sources to the total BVOC budget and the dynamics of long-term BVOC pools in vegetation.

1.2.1 Terpenes

Terpenes are BVOCs formed of five-carbon isoprene units. Isoprene emissions from terrestrial vegetation are considerable, and it has the largest global annual budget (516 Tg C) of non-methane BVOCs, (average of various models, Arneth et al. 2008). Monoterpenes consist of two isoprene units (10 carbon atoms) (Figure 1) whereas sesquiterpenes contain three of them (15 carbon atoms). Monoterpenes are among the second most emitted non-methane BVOCs, with a global annual budget of 91 Tg C (average of various models, Arneth et al. 2008). Monoterpene emissions are pronounced over conifer-dominated forests, such as boreal forests, because conifer trees can store monoterpenes in resin. Sesquiterpene emissions from terrestrial vegetation are also large, but sesquiterpene emission budgets and sources remain relatively uncertain because of their low volatility and high reactivity, and consequent difficulties in measuring them (Kim et al. 2009). The larger terpenes, such as resin acids that contain four isoprene units (Figure 1), have low volatility and are not commonly studied among VOCs.

This thesis mainly discusses monoterpenes, as they form a large part of the resin and are an important part of the BVOC budget of boreal forests. Monoterpenes are mainly defence and signalling compounds, and in addition to the defence against biotic stresses described earlier (section 1.2.2), monoterpenes may increase plant resilience to abiotic stresses. For example, monoterpenes may help reduce dangerous oxidation reactions in leaves that are exposed to heat (Loreto et al. 1998).

Monoterpenes are produced in the plastids of living cells, especially in the epithelial cells of resin-producing conifers (Turner et al. 2019). Monoterpene production is limited by enzymatic regulation and substrate availability controlled by temperature and light, and it also depends on phenology and tissue maturity, at least in the leaves (Vanhatalo et al. 2018). Upon production, monoterpenes can be stored in long-term storages, such as resin in conifer trees, or in temporary storages, such as cell membrane lipids (Niinemets and Reichstein 2002; Noe et al. 2006), or they can be emitted instantly (*de novo* emissions). The size and composition of a monoterpene storage in a pine needle, for example, may vary either because of new production or emissions from the storage. The variation is often small (Llusià et al. 2006; Vanhatalo et al. 2018), probably due to long storage turnover times, but larger changes in monoterpene storage are possible during needle development (Thoss et al. 2007). Monoterpene production and storage affect the emissions of monoterpenes, but the emissions also depend on temperature and other rapid changes in the environment. A large part of the monoterpene emissions from needles are *de novo* emissions (Ghirardo et al. 2010; Harley et al. 2014) and another part may originate from both long-term and temporary storages (Niinemets and Reichstein 2002; Noe et al. 2006), meaning that the total emissions are

combined emissions of stored compounds and recently produced compounds. As a result, considerable differences may occur between the composition of monoterpenes that are produced, stored and emitted, and these interrelations are further complicated by the varying time lags in the different processes (Vanhatalo et al. 2018).

Monoterpene emissions may also diverge from the storage and production because of the different volatilities of the various monoterpene compounds (Table 1). Volatility describes how easily a substance vaporises, and it is regulated by the vapour pressure of the compound. In the case of BVOCs, partitioning between water and air, described by the Henry's law constant, and between water and lipid phases, described by the octanol/water partition coefficient, also affect the overall volatility from plant structures to the ambient air. The vapour pressures of various monoterpenes vary considerably (Hoskovec et al. 2005; Rumble et al. 2017; Kim et al. 2018). For example, α-pinene is highly volatile with a vapour pressure of 663 Pa at 25 °C whereas terpinolene has a smaller vapour pressure of 99 Pa at 25 °C (Kim et al. 2018) (Table 1). Monoterpenes are generally insoluble in water, but certain oxygenated monoterpenes (monoterpenoids), such as linalool, are moderately water-soluble (Copolovici and Niinemets 2005; Noe et al. 2006) (Table 1). These differences in vapour pressure and solubility affect the spectrum and dynamics of monoterpene emissions measured from plants so that compounds with higher vapour pressure may be pronounced in emissions compared to their proportions in storage. In addition, the emissions of water-soluble compounds are more controlled by stomatal conductance than emissions of non-water-soluble compounds.

Table 1. Chemical properties of certain compounds studied in this thesis

	Molecular mass ($g\ mol^{-1}$)	Henry's law coefficient ($Pa\ m^3\ mol^{-1}$, at 25 °C)	Octanol/ water partitioning coefficient ($mol\ mol^{-1}$, at 25 °C)	Vapour pressure (Pa, at 25 °C)
Monoterpenes				
α-pinene	136.24	13 600	30 900	663
β-pinene	136.24	6 830	26 300	391
Δ^3-carene	136.24	13 640	40 740	496
terpinolene	136.24	2 600	29 510	99
Monoterpenoids				
linalool	154.25	2.09	933	21
OVOCs				
methanol	32.04	0.461	0.170	16 900
acetaldehyde	44.05	7.00	0.457	120 300
acetone	58.08	3.88	0.575	30 900

Sources: https://pubchem.ncbi.nlm.nih.gov (visited in 22.6.2019), Niinemets and Reichstein 2002, 2003, Copolovici and Niinemets 2005, references therein

1.2.2 Resin effects on monoterpene emissions

Resin is a large pool of monoterpenes and sesquiterpenes in conifer trees, thus its composition may be expected to affect the emissions of these compounds. As discussed earlier (section 1.1.1), the tree-to-tree variation in resin composition is considerable even within the same species (e.g. Marpeau et al. 1989; Latta et al. 2000; Fäldt et al. 2001; Thoss et al. 2007; Kännaste et al. 2013). Similar tree-to-tree variation has been reported in monoterpene emissions from pine shoots (Komenda and Koppmann 2002; Bäck et al. 2012; Semiz et al. 2012), but whether the emitted monoterpenes correspond to the monoterpene spectrum in resin remains unclear. If resin composition and monoterpene emissions correlate closely, resin sampling could be an easy and fast way to map the monoterpene emission variability within a population or species. For example, Flores and Doskey (2015) used information on resin composition and the various chemical characteristics of the resin compounds to estimate the emissions of terpenes and terpenoids from *Pinus strobus* (L.) shoots. This kind of information would be useful as atmospheric chemistry models evolve to account for the diverse monoterpenes.

When modelling and quantifying the monoterpene emissions from conifers, even when considering the effects of resin composition (Flores and Doskey 2015), resin is often considered a passive pool from which the compounds evaporate in a temperature-dependent manner (e.g. Tingey 1980), with potential effects of other variables such as humidity (Tingey et al. 1991; Llusià and Peñuelas 1999). However, resin is not passive. On the contrary, its pressure and flow vary according to temperature and water potential in stem, and the effects of these resin dynamics on the monoterpene emissions from foliage and stem are unknown.

In addition to the potential effects of resin dynamics within a tree, resin that is exposed may temporarily alter the stand-level emissions of monoterpenes. On the one hand, cutting conifer trees exposes the stored resin, thus forest management practices may have large, yet relatively short-term effects on stand-level monoterpene budgets (Schade and Goldstein 2003; Räisänen et al. 2008; Haapanala et al. 2012; Kivimäenpää et al. 2012). On the other hand, naturally exposed resin on developing cones, buds and the bases of needles may contribute up to 10% of the total ecosystem monoterpene flux while the resin is fresh (Eller et al. 2013). An extreme effect of resin may be observed in pine forests that are used for resin tapping, where emissions from resin may dominate the emissions from foliage (Pio and Valente 1998). Finally, bark beetles cause resin leakage, which probably contributes to the increased emissions of monoterpenes that have been detected in bark beetle-infested forests (Berg et al. 2013).

1.2.3 Water-soluble oxygenated VOCs

Methanol, acetaldehyde and acetone are among the most common oxygenated volatile organic compounds (OVOCs) measured from vegetation (Fall 2003). Estimates for global annual biogenic emissions range between 38–107 Tg C for methanol (Fall 2003; Messina et al. 2016), 44–88 Tg C for acetaldehyde (Fall 2003) and 25–59 Tg C for acetone (Fall 2003; Messina et al. 2016). These compounds are emitted as side products of plant metabolism, but all their sources and possible functions are not yet fully understood.

Methanol is mainly produced during plant growth: it is released in demethylation when the pectin of cell walls is formed or degraded during the growth and senescence of plant tissues (Nemecek-Marshall et al. 1995; Fall and Benson 1996; Galbally and Kirstine 2002; Hüve et al. 2007; Seco et al. 2007). Thus, it is produced in all growing plant parts. Some methanol is also released during protein methyl transferase and protein repair processes, and in the soil during the degradation of plant material (Fall and Benson 1996).

High methanol and acetaldehyde emissions, in particular, occur when the soil is flooded and tree roots lack oxygen (O_2) (Holzinger et al. 2000; Kreuzwieser et al. 2000; Karl et al. 2003; Copolovici and Niinemets 2010; Bracho-Nunez et al. 2012). Acetaldehyde emission peaks are explained by anoxic metabolism in plant roots that produces ethanol that is further oxidised into acetaldehyde (Seco et al. 2007). However, ethanol and acetaldehyde emissions have also been measured during low soil moisture (Schade 2002), indicating that other important sources exist. Ethanol formation and acetaldehyde emissions may also result from insufficient diffusion of (O_2) and anoxia in the stem, especially during fast growth and high metabolic activity (Kimmerer and Stringer 1988). Like methanol, acetaldehyde is also produced during plant material degradation in the soil (Warneke et al. 1999). In addition, the decarboxylation of pyruvic acid in leaves exposed to rapid light-dark transitions cause the release of acetaldehyde and large emission bursts (Karl et al. 2002, 2003; Hayward et al. 2004; Karl 2004; Seco et al. 2007; Jardine et al. 2012).

The VOC emission bursts after a light-dark transition also contain acetone (Jardine et al. 2012). Acetone has been proposed to be a side product of hydrogen cyanide and a product of acetoacetate carboxylation in soil bacteria (Fall 2003; Seco et al. 2007), but its main sources and its role in plants are not well known.

Methanol, acetaldehyde and acetone are all water-soluble with small Henry's law coefficients (Table 1). Thus, they can enter the water films in leaves and the xylem sap in the roots and stem, and their emissions from shoots are considered to be controlled by stomatal conductance (Niinemets and Reichstein 2003; Niinemets et al. 2004; Harley et al. 2007). Evidence also shows that methanol and acetaldehyde, along with its precursor ethanol, can be transported in the xylem sap from the soil and stem to the leaves (Kreuzwieser et al. 2001; Grabmer et al. 2006; Folkers et al. 2008). Consequently, the emissions measured from the leaves may partly originate from the soil, roots and stem due to transport. However, the magnitude and importance of the OVOC transport in total shoot emissions is still unknown, and the transport mechanism has not been studied in field conditions.

1.2.4 VOC emissions from stem

The BVOC emissions from trees are most commonly measured from the foliage because it is considered the most active part of the tree. This is reasonable when studying compounds, such as isoprene, that are tightly linked with metabolism that occurs only or mainly in the leaves. However, for example monoterpenes, methanol and acetaldehyde are also synthesised in and transported from other parts of a tree, and in the case of monoterpenes, even stored in large quantities in other parts of the tree.

The relatively few studies on conifer stem BVOC emissions have measured the effects of fungal infection or insect damage on the emissions and the volatile cues that the stem sends to bark beetles (Rhoades 1990; Gara et al. 1993; Heijari et al. 2011; Amin et al. 2012, 2013; Lusebrink et al. 2013; Kovalchuk et al. 2015; Ghimire et al. 2016). Ethanol and monoterpene emissions from the stem reportedly increase due to various biotic stresses (Gara et al. 1993; Amin et al. 2012, 2013; Lusebrink et al. 2013; Ghimire et al. 2016). When the stress is targeted to the stem, the stem emissions increase more than the emissions from the foliage (Heijari et al. 2011; Amin et al. 2012). Abiotic stresses may also affect the emissions from the stem: when subjected to drought, total monoterpene emissions from the stem of lodgepole x jack pine hybrids increased (Lusebrink et al. 2013). Including stem BVOC emissions into the context of the whole stand BVOC emissions for the first time, Vanhatalo (2018) calculated that the unwounded stems of Scots pine (*Pinus sylvestris* L.) trees contributed approximately 2% of the total stand BVOC emissions, while the foliage made up the largest part. Although 2% is a small proportion, omitting it will cause a bias when calculating

emission sums over longer periods. Furthermore, the proportion of stem emissions probably varies considerably depending on the basal area, tree species, forest age and environmental conditions or stresses, but similar estimates from other forests are not yet available.

Measurements on short and long-term VOC emission dynamics from the tree stem are quite rare. Temperature has been reported to drive monoterpene and methanol emissions from pine stems on at least a daily scale (Vanhatalo 2018; Staudt et al. 2019). However, this effect may be different on a longer time scale: Staudt et al. (2019) reported largest monoterpene emissions from a Maritime pine (*Pinus pinaster* Ait.) stem during humid rather than warm days. Stem monoterpene emissions also depend on phenology: the onset of transpiration and change from the winter to summer state in the stem caused large monoterpene emission peaks from the stem (Vanhatalo et al. 2015). In addition, the diverging enantiomeric compositions of α- and β-pinene emissions between the shoots and stem indicate differences in their production between the different tree parts (Staudt et al. 2019). Thus, we can assume that BVOC emissions from the stem do not follow exactly the same patterns as the emissions from shoots. Yet the environmental or physiological factors that drive stem emissions are poorly understood compared to shoot emissions.

2 MOTIVATION AND OBJECTIVES

A Scots pine stem is both a considerable storage and source of VOCs, but our understanding of stem VOC emission dynamics, drivers and spatial variability is too limited to include them into stand-level modelling. In addition, the functioning of resin, i.e. the major monoterpene pool and important defence mechanism, has been little studied in the moist boreal environment. Considering the environmental changes, understanding the drivers of resin dynamics is needed to predict the challenges for tree defence.

In this dissertation, I studied the effects of temperature and tree water relations and transport on the resin pressure dynamics and BVOC emissions from Scots pine. The overall aim was to clarify the relationships between tree physiology – with special attention to tree water relations – resin dynamics and composition, and BVOC emissions from mature tree stems and foliage, in field conditions.

The specific objectives were to

1) describe the temporal dynamics and environmental and physiological drivers of resin pressure both at a diurnal and day-to-day scale (studies I, II)

2) compare the spatial patterns of resin pressure and composition with monoterpene emission patterns from the foliage (study II)

3) analyse the dynamics of monoterpene emissions as a function of resin pressure (study I) and the dynamics of monoterpene and OVOC emissions as a function of soil moisture and tree water status (study III)

4) study the transport of water-soluble VOCs – methanol, acetone and acetaldehyde – in the xylem sap and the role of transport in their emissions from the foliage (study IV) and stem (study III)

3 METHODS

3.1 Study site

All field measurements were conducted between 2011 and 2017 at the SMEAR II station (Station for Measuring Ecosystem-Atmosphere Relation) located in Hyytiälä, southern Finland. The measurement forest is dominated by mature Scots pines, regenerated by sowing after prescribed burning in 1962. The dominant trees during the measurements were approximately 18–20 metres tall. Other stand species include Norway spruce (*Picea abies* (L.) Karst.), especially in the undergrowth, downy birch (*Betula pubescens* Ehrh.), silver birch (*Betula pendula* Roth) and trembling aspen (*Populus tremula* L.). The understorey vegetation contains mosses and dwarf shrubs: bilberry (*Vaccinium myrtillus* L.) and lingonberry (*Vaccinium vitis-idaea* L.). The soil is of medium fertility haplic podzol. The long-term mean temperature in the forest is 3.5 °C and yearly rainfall is 711 mm (Ilvesniemi et al. 2010; Pirinen et al. 2012).

The matter and energy fluxes between the various parts of the ecosystem and between the ecosystem and atmosphere have been studied at the SMEAR II station since 1995 (Hari and Kulmala 2005). Research consists of micrometeorological measurements and gas and trace gas fluxes using the eddy covariance techniques and enclosures dedicated to measure gas fluxes from soil, understorey vegetation, tree shoots and the stem. In addition, continuous measurements are available on soil conditions, including moisture, temperature and water potential.

3.2 Resin measurements

3.2.1 Resin pressure

Scots pine resin pressure in studies I and II was measured with a system modified from Vité (1961). First, a 3-mm hole was drilled slightly tangentially to the tree stem, approximately 4 cm into the xylem. Then, a 3-mm metal tube was pushed into the hole, approximately 3 cm deep, and the other end of the tube was connected to a pressure gauge (Wika 111.16.40.16, Klingenberg, Germany) (studies I and II) or to a pressure transducer (Gems Sensors 3100, Plainville, USA) (study II) (Figure 4). The hole, the tube and the pressure gauge or transducer cavity were filled with glycerine to transmit the changes in resin pressure and to prevent resin flowing into the gauge or transducer. The connection between the stem and the metal tube was sealed with silicone, but the small quantity of spilt-over resin also formed a good seal.

Because the resin tended to crystallise inside the hole and the metal tube, the pressure measurement mechanism needed to be reinstalled every two to three weeks. The crystallisation and the potential decreasing defence reaction following the wounding often caused a general, decreasing trend in resin pressure over the two-to-three-week measurement periods. In study I, mainly investigating the short-term dynamics, this trend was corrected if necessary by using the residuals of a linear function of time. In study II, where long-term trends were also studied, data both with and without trend correction were used because the actual trends and the trend caused by the measurement could not be separated.

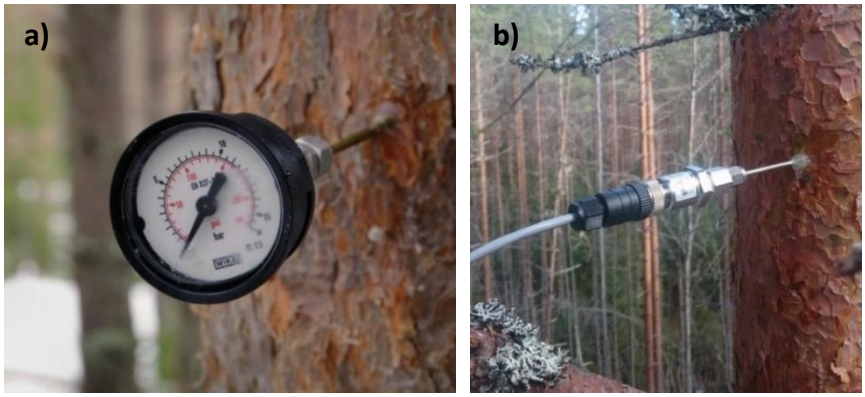

Figure 4. a) pressure gauge (used in studies I and II) (photo by Juho Aalto), and b) pressure transducer (used in study II) attached to a Scots pine (*Pinus sylvestris*) stem (photo by Kaisa Rissanen)

3.2.2 Resin composition

In study II, the monoterpene composition of resin was measured using a gas chromatograph-mass spectrometer (GC-MS), which contains two phases of molecular separation: the capillary column of the GC and the ionisation and fragmentation of the MS, enabling separation of the compounds with similar ion mass and similar retention time in the GC capillary. The monoterpene composition was analysed from approximately 3-mg resin samples that were collected from small wounds punched into the xylem surface of 16 sample trees. The samples were collected rapidly after the first resin droplets appeared on the wound, and after weighting they were dissolved in heptane to avoid the loss of volatile components. The samples were analysed by an Agilent 6890 N gas chromatograph connected with an Agilent 5975 mass selective detector (Agilent Technologies, Palo Alto, CA, USA). Each sample contained an internal standard Decane-d22 and standard solutions were used to calibrate for mass spectrums and retention times. Quantification of the monoterpene concentrations was made by calculating the area of the ion chromatogram peak of the base ion of each compound.

3.3 Resin dynamics modelling

In study II, the temperature dependence of resin pressure was modelled using the information on resin monoterpene composition (see above, section 3.2.2) and COSMOtherm software. COSMOtherm calculates the properties of liquids that consist of several compounds based on the COSMO-RS (Conductor-like Screening Model for Real Solvents) theory (Klamt et al. 1998), and it is generally used in predicting the characteristics of industrial solvents. COSMOtherm calculated the density of three resin mixtures – with high, intermediate and low monoterpene contents – at various temperatures. The thermal expansion of resin and the resulting pressure changes could be calculated based on the density changes. In addition, COSMOtherm calculated the solubility of carbon dioxide (CO_2), nitrogen (N_2) and O_2 in the three resin mixtures and at various temperatures. Based on this information, the volume and growth of potential gas bubbles within the resin and consequently the change in total resin volume and resulting pressure change could be estimated. Finally, COSMOtherm calculated the vapour pressures of resin at various temperatures. These three temperature-related effects were combined to explain the diurnal temperature dependence of resin pressure.

3.4 VOC emission measurements

3.4.1 Continuous VOC emission measurements

The continuous VOC emissions measurements from both Scots pine shoots and stems were based on a chamber system, where chambers attached around the shoots, stem and soil are cyclically measured and flushed (Kolari et al. 2009, 2012; Aalto et al. 2014; Aalto 2015; Vanhatalo et al. 2015; Vanhatalo 2018). The chambers used in this study consisted of dynamic shoot chambers (study IV), steady-state stem chambers (studies I, III and IV) and dynamic stem chambers (study III).

The dynamic shoot chambers (Figure 5 a) were built of FEP-coated (fluorinated ethylene propylene) acrylic plastic and they enclosed top-canopy pine shoots, the buds of which had been removed the previous year to eliminate the effect of growth on the emission dynamics. For the measurement, one chamber at a time was automatically closed, and sample air was drawn from it to the gas analysers. Sample air was replaced by ambient air that leaked through the small holes of the chamber. While the chamber was not measured, it remained open for flushing.

The steady-state stem chambers consisted of a polyethylene-coated aluminium spiral tube around the tree stem and FEP foil tightened around the stem and the spiral tube, closed from the top and bottom with elastic bands (Figure 5 b). Openings for incoming replacement air and outgoing sample air were the only openings in these chambers. When the chamber was being measured, a sample air flow of 1 l/min was drawn from the chamber into the analysers and replaced with a slightly larger flow of ambient air. When the chamber was not being measured, a 0.4-l/min flow of ambient air was maintained through it for flushing.

Figure 5. Chambers for measuring VOC emissions and H_2O and CO_2 exchange from shoots and stem of a Scots pine (*Pinus sylvestris*). a) Dynamic shoot chamber (photo by Juho Aalto), b) steady-state stem chamber (photo by Juho Aalto) and c) dynamics stem chamber (photo by Kaisa Rissanen).

The dynamic stem chambers (Figure 5 c) were built of aluminium pieces around the tree stem and a FEP foil tightened around the stem and the aluminium pieces, closed from top and bottom with elastic bands. Two of the pieces on opposite sides of the stem had automatically opening and closing lids and fans that helped circulate air through the chamber during and between the measurements. For measurement, the chamber lids were automatically closed, 1 l/min of sample air was drawn from it to the analysers, and the sample air was replaced with a slightly larger flow of ambient air. When the chamber was not measured, a 0.4-l/min flow of ambient air was maintained through the open chamber for flushing. In most chambers, the temperature within the chamber was recorded with copper-constantan thermocouples.

A proton transfer reaction-mass spectrometer (PTR-MS, IONICON Analytic GmbH, Innsbruck, Austria), a commonly used instrument for high-frequency online VOC measurement, was used for measuring the VOC concentrations in the sample air drawn from the chamber. Sample air was drawn into the PTR-MS at a rate of 0.1 l/min. In the high vacuum of the PTR-MS reaction chamber, H_3O^+ ions give their proton to the sample air molecules (proton-transfer reaction). This is a gentle ionisation method that causes relatively little fragmentation of the molecules, but it works only for compounds that have higher proton affinity than water. In the quadrupole PTR-MS used here, the ions are then separated by quadrupole and led to a secondary electron multiplier and finally to a detector. As the quadrupole filters the ions by their mass-to-charge ratio, various compounds with similar ionised mass cannot be separated in this system. Here, ionised masses (amu) 137, 33, 45 and 59 were measured, corresponding to monoterpenes, methanol, acetaldehyde and acetone.

Instrument sensitivities to certain masses were known based on calibrations made with standard gas every two or three weeks, and the concentrations in sample gas could be calculated from the measured detector counts (Taipale et al. 2008). The concentrations of enclosure air were calculated into emissions using a mass balance equation (Equation 1) in case of the dynamic chambers.

$$C(t) = C_0 + \left(\frac{C_{in} - C_0}{V} + \frac{E}{F}\right)\left(1 - e^{\frac{-Ft}{V}}\right) \quad \text{(Equation 1)}$$

C(t) is the concentration of the compound in the chamber as a function of time (t), C_{in} is the concentration of replacement air, C_0 is the concentration of the ambient air, F is the airflow through the chamber, v the chamber volume and E the emission rate that was found by fitting the equation to the concentration increase during chamber closure (Hari et al. 1999; Kolari et al. 2012). Emissions for the steady-state chambers were calculated as the difference between the chamber concentration in the steady state and the ambient air concentration, multiplied by the air flow through the chamber.

In high relative humidity, water vapour may condense on the chamber walls, tubing and enclosed surfaces. These water films may adsorb water-soluble OVOCs methanol, acetaldehyde and acetone, thus OVOC data were omitted when the relative humidity in the chamber was above 70–75% (Altimir et al. 2006).

3.4.2 VOC emission potential

To achieve comparable VOC emission values from various environments the emissions are often normalised to standardised conditions (for example, temperature 30 °C and photosynthetic photon flux density 1000 μmol m^{-2} s^{-1}). If the measured compounds mainly originate from pools, for example, monoterpene emissions from conifers, the emissions are normalised only to temperature (Guenther et al. 1993; Guenther 1995) (Equation 2).

$$E = E_0 * e^{[\beta(T-T_S)]} \qquad \text{(Equation 2)}$$

E is the measured emissions, E_0 is the emission potential, β is an empirical parameter describing the temperature sensitivity of the emissions (often a global average 0.09 K^{-1} is used), T is the temperature in the chamber and T_S is the standard temperature (30 °C or 303 K). This normalisation removes the short-term effect of temperature on the vapour pressures and evaporation of the VOC compounds from the data and gives a baseline emission value called the emission potential.

The emission potentials of monoterpenes, methanol and acetaldehyde were calculated in study III to analyse the effects of various environmental variables such as tree water relations on temperature-normalised stem emissions. However, instead of using the β-parameter fixed at 0.09 K^{-1}, β-parameter was fitted in three-day windows. This aimed to account for the temperature sensitivity changes over the growing season and variation between different years, trees and compounds.

3.4.3 Point measurements of VOC emissions from shoots

In study II, the monoterpene composition of Scots pine shoot emissions was measured from the cut branches of 16 sample trees similarly as described in Bäck et al. (2012). The branches were collected with a long pole branch cutter from the lower canopy. After approximately one week of storage in the dark, at + 4 °C, the cut shoots were taken to room temperature and after short acclimation installed for measurement into FEP foil bags. 0.2 l/min of air that was purified from VOCs and oxidants with an activated carbon trap and manganese dioxide-coated copper net was led into the bag and both incoming and outgoing air were sampled into Tenax TA - Carbopack B adsorbent tubes. In the laboratory, the adsorbed VOCs were released by a thermal desorpter (PerkinElmer TurboMatrix 650, Waltham, USA) and measured using a gas chromatograph (PerkinElmer Clarus 600, Waltham, USA) connected with a mass spectrometer (PerkinElmer Clarus 600T, Waltham, USA). Six standard samples with various concentrations of the studied analytes were used for calibrations. Emission values were calculated based on steady-state measurements as a difference between the incoming and outgoing sample concentration multiplied by the flow rate through the sample bag.

Table 2. Resin and BVOC measurements in each study of the thesis

Measurement	Method	Study I May–August 2013	Study II June–August 2017	Study III June–August 2013, 2015 & 2017	Study IV May–August 2010, 2011, 2013, 2014 & 2015
Resin pressure	Pressure gauge	5 trees	10 trees		
Resin composition	GC-MS		16 trees		
Monoterpene emissions from stem	PTR-MS	1 tree		3 trees	
Monoterpene composition in shoot emissions	GC-MS		16 trees		
OVOC emissions from shoots	PTR-MS				3 trees
OVOC emissions from the stem	PTR-MS			3 trees	

3.5 Tree water status and CO_2 efflux measurements

Measurements on water potential, transpiration and growth were used to analyse the effects of tree physiology and especially tree water status on the resin dynamics and VOC emissions. In studies I and III, tree water status was observed using linear displacement transducers as point dendrometers (Solartron Inc., Model AX/5-0/5, Bognor Regis) (Figure 6). They measure changes in the whole stem or xylem diameter that are functions of growth (irreversible) or changes in stem water status (reversible). A decreasing water potential reduces the stem diameter because it causes both shrinkage of the water-conducting tracheids and a decrease in turgor pressure in the living parenchyma cells in the sapwood (Irvine and Grace 1997; Perämäki et al. 2001; Mencuccini et al. 2013; Lintunen et al. 2017). As radial stem growth occurs in the cambial zone, diameter variations measured from the xylem beneath this zone only reflect changes in water status. Measuring the stem diameter both from the xylem and on the bark enables separating the growth signals (Chan et al. 2016).

In addition, transpiration measurements were used to analyse the effect of transport on the OVOCs emissions of (studies III and IV) and CO_2 efflux measurements from the stem were used to describe the metabolic activity in the stem (study III). Transpiration was measured by the shoot chamber system described above (section 3.4.1) and by Kolari et al. (2012) and stem CO_2 flux using the stem chambers described above (section 3.4.1) and by Vanhatalo (2018). For analysis of water and CO_2 concentrations, the sample air from the chambers was drawn to a URAS 4 infrared light absorption gas analyser (Hartman and Braun, Frankfurt am Main, Germany) or to a Li-840 A gas analyser (Li-Cor, Lincoln, NE, USA). Like VOC emissions, the water and CO_2 fluxes were calculated using the mass balance equation (Equation 1) or their steady-state concentrations, depending on chamber type. Because of water condensation forming on the chamber surfaces in high relative humidity, the water and CO_2 flux measurements were unreliable when relative humidity exceeded 70–75% and these measurements were removed prior to analysis.

Figure 6. Linear displacement transducers for continuously measuring small changes in the xylem and bark diameter

3.6 Path analysis as a tool for separating variable interactions

In studies I and IV, two path analysis approaches were used to compare and distinguish the simultaneous effects of different variables on the monoterpene emissions from the stem (study I) or the OVOC emissions from the shoots (study IV). In study I, explanatory framework-based regression analysis (EFRA) was employed to compare the effects of resin pressure and temperature on the stem emissions of monoterpenes. The method was based on simple regressions, so that first the coefficients of temperature and resin pressure effects on monoterpene emissions were calculated separately (Figure 7 a, line 1) and then their coefficients were calculated in a model where they both explained monoterpene emissions (Figure 7 a, line 2). The changes in their coefficients gave indications on the roles of the two variables in explaining the emissions and whether and how much the effect of temperature was mediated through resin pressure.

A simple form of structural equation model (SEM) was employed to clarify the interactions between temperature, stomatal conductance and transpiration in explaining the emissions of OVOCs from the shoots. The calculations were made in R lavaan package (Rosseel 2012). The path analysis described the causal relations between independent variables (temperature and stomatal conductance) that explained the dependent variable (OVOC emissions) (Figure 7 b, line 1), possibly through another dependent variable (transpiration) (Figure 7 b, line 2). The interrelations between the variables and the importance of each variable were estimated by their coefficients in each regression and the significance (p-value) of each coefficient.

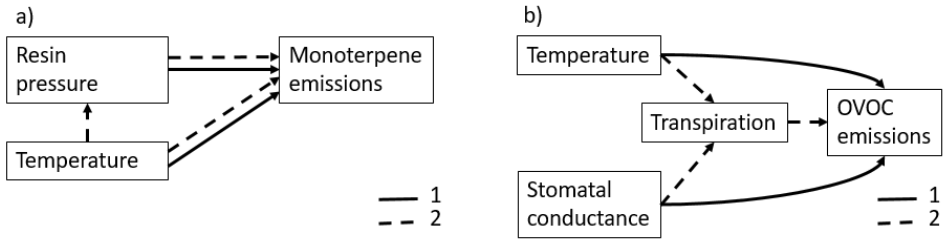

Figure 7. a) Framework of the EFRA approach, where first the individual effects of resin pressure and temperature on monoterpene emissions were calculated (1) and then their effects when both variables were explaining monoterpene emissions (2) and b) framework of path analysis, where the effects of temperature and stomatal conductance on OVOC emissions were calculated (1) and then transpiration was added to the model (2).

4 RESULTS AND DISCUSSION

4.1 Resin pressure dynamics

4.1.1 Resin pressure as a function of temperature and tree water status

Unlike expected based on the previous studies from dry environments, studies I and II showed that in the moist and cool boreal environment the diurnal resin pressure dynamics of Scots pine followed temperature (Figures 8 and 9). Resin pressures were highest in the daytime, between 13.00 and 15.00, whereas the lowest pressures occurred at dawn, between 03.00 and 06.00. This pattern was similar regardless the measured tree or the phase of growing season.

The strong control of temperature on resin pressure was explained in study II by two processes: 1) thermal expansion increases resin pressure and 2) increasing temperature decreases gas solubility (for example, N_2, O_2 and CO_2) in the resin, which allows these gases to move to the gas phase and enlarge bubbles in the resin, increasing resin pressure. Although in study I, the monoterpene vapour pressure changes were suggested as one reason for the strong temperature regulation, the changes in vapour pressures were too small to contribute to the daily dynamics of resin pressure. Correspondingly, Pio and Valente (1998) found that changes in vapour pressure solely could not explain the temperature dependence of monoterpene emissions from exposed resin.

Despite the strong temperature dependence at a daily scale, temperature did not explain all variation in resin pressure. In study I, resin pressure sometimes deviated from the diurnal temperature dynamics, especially when the ambient vapour pressure deficit (VPD) changed suddenly. In addition, over some of the 5–8-day measurement periods, the residuals of a temperature model explaining resin pressure correlated positively with xylem water potential inferred from the xylem diameter change measurements (study I) (Figure 9). Moreover, in study II, resin pressure trends over the growing season followed the soil water potential whereas the long-term effect of temperature was negative (Figure 9). These diurnally small, but in the longer term important impacts of the xylem and soil water potential on resin pressure also showed an effect of water relations on resin pressure in the boreal environment, as shown in drier regions by Bourdeau and Schopmeyer (1958), Vité (1961), Lorio and Hodges (1968b) and Helseth and Brown (1970). However, this impact seems to mostly be overshadowed by the strong temperature impact.

4.1.2 Resin pressure dynamics in moist and dry environments

Based on the results presented above (section 4.1.1), resin pressure follows the diurnal patter of temperature in a moist environment (Figure 8), but follows the diurnal changes in xylem water potential in dry environments and inversely the changes in transpiration rate and VPD (Bourdeau and Schopmeyer 1958; Vité 1961; Barret and Bengtson 1964; Lorio and Hodges 1968a; Neher 1993). This difference in the daily dynamics of resin pressure between dry and moist sites suggests either that the availability of water strongly shapes the resin pressure dynamics between these different environments or that the measurement techniques for resin pressure were considerably different between the measurements.

Considering the first option, Vité, (1961) reported that the effect of VPD on resin pressure was weaker when water availability in the soil was high and stronger when the soil was dry. Drought conditions are very rare in Hyytiälä, Finland, and water availability was high during the measured years: in study I, soil water potential varied between 0 and -500 kPa during the

resin pressure measurements, and between 0 and -25 kPa in study II. Thus, the high water availability in these measurements should weaken the effect of VPD and water potential on resin pressure. Moreover, the daily range of resin pressure measured in a drought-prone environment is considerably larger (approximately 4 bars) (Lorio and Hodges 1968b) compared to a moist environment (0.5–1 bar) (Figure 8). Thus, VPD, transpiration and water potential probably do not affect the tracheid sizes and turgor pressures of epithelial cells strongly enough in moist conditions and in the short term to overcome the temperature effect on resin pressure. In the longer term, however, the slow changes of water status in the tracheids and epithelial cells may be large enough to impact resin pressure. At an even longer time scale, acclimation and the adaptation of trees to a certain climate might even affect resin duct responsiveness, rigidity and permeability.

Considering the second option concerning the different measurement techniques, the methods used in studies I and II were tested in a drought-prone Scots pine forest (Pfynwald) standing on sandy soil in Switzerland. In Pfynwald, resin pressures followed a diurnal pattern with maximum levels recorded at dawn and minimum levels in the afternoon (unpublished data) (Figure 8), corresponding to results from dry regions (Bourdeau and Schopmeyer 1958; Vité 1961; Lorio and Hodges 1968b; Helseth and Brown 1970; Neher 1993). Moreover, the long-term resin pressure dynamics in the Pfynwald forest followed the soil water potential trends, decreasing towards the end of the growing season. Based on these results from a dry environment that corresponded to earlier studies, the methods used in studies I and II were considered valid.

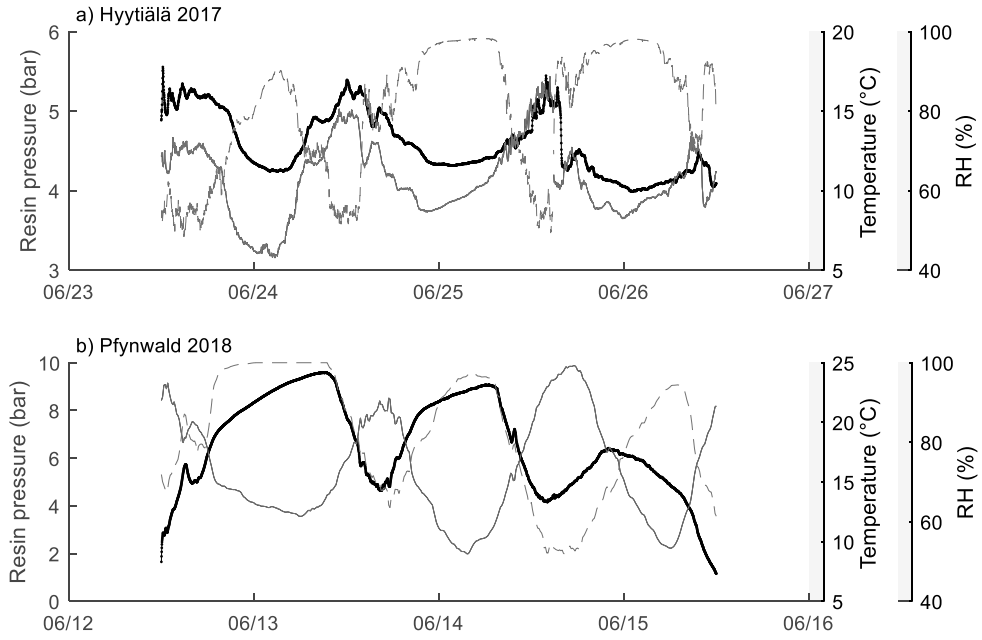

Figure 8. Variation in resin pressure (solid black), ambient temperature (solid grey) and relative humidity (dashed grey) a) in a moist, boreal Scots pine (*Pinus sylvestris*) forest in Hyytiälä, Finland (study II) and b) in a dry inner-alpine Scots pine forest in Pfynwald, Switzerland (unpublished data).

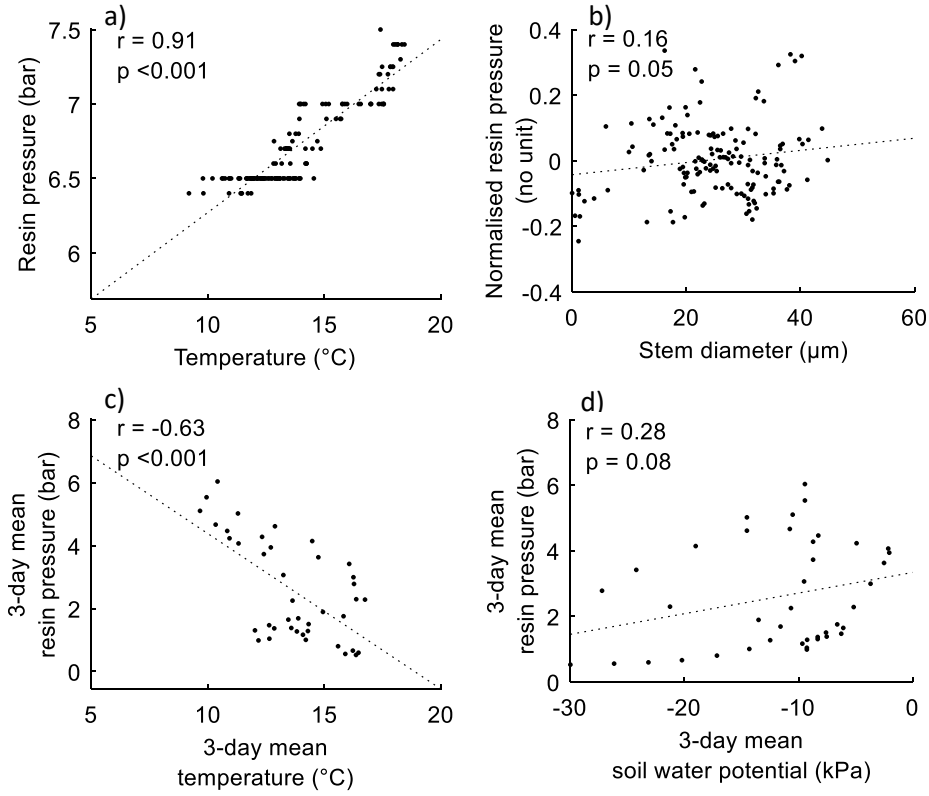

Figure 9. Correlations between a) trend-corrected resin pressure and temperature, b) temperature-normalised resin pressure and xylem diameter in Scots pine (*Pinus sylvestris*), in Hyytiälä, July 15–18, 2014 (study I), c) 3-day mean of resin pressure and temperature and d) 3-day mean of resin pressure and soil water potential in Scots pine, in Hyytiälä, June–July 2017 (study II). Dashed lines present the least-square fit.

4.1.3 Resin pressure dynamics in different stem parts

Although resin pressure dynamics corresponded between all measured trees, differences existed between the tree parts. Resin pressures were higher in the top part versus the bottom part of the stem at the beginning and end of the growing season, while being higher in the bottom part of the stem in mid-summer (study II). The differences between the top and bottom parts were largest when the water potential in the xylem was below average and transpiration was high (study I). Transpiration decreases water potential proportionally more in the top part of the stem than in the bottom part, which may explain the lower resin pressure in the top part of the stem during periods of high transpiration.

4.2 Resin effects on monoterpene emissions

4.2.1 Resin pressure and monoterpene composition compared to monoterpene emissions from the shoots

As resin is a large pool of monoterpenes in conifer stems and shoots, resin composition may be expected to affect the composition and tree-to-tree variation of emitted monoterpenes. Indeed, study II showed that the stem resin and shoot emissions of 16 measured Scots pines contained the same monoterpenes in roughly corresponding proportions (Figure 10). The most abundant compounds were α-pinene, Δ^3-carene and β-pinene, with smaller quantities of limonene, terpinolene, camphene and p-cymene.

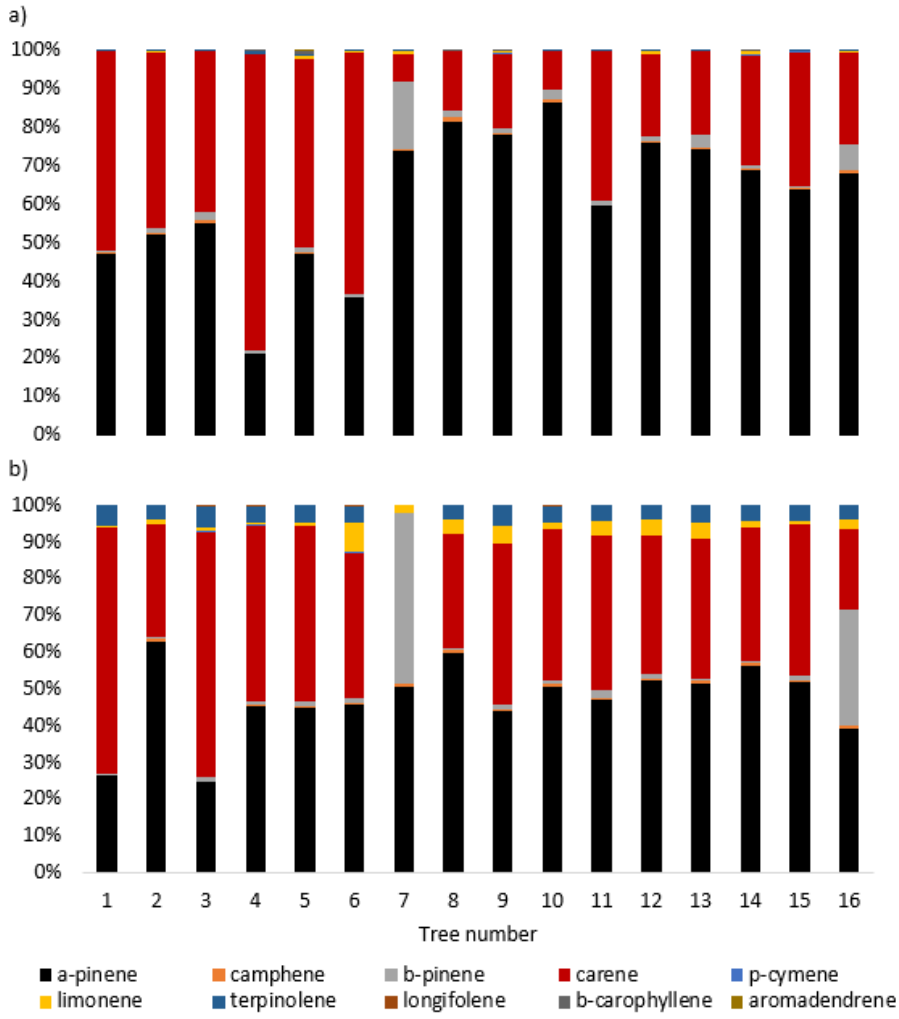

Figure 10. Monoterpene spectrum in the a) shoot emissions and b) stem resin of 16 Scots pines (*Pinus sylvestris*) in Hyytiälä, August 2016

However, the monoterpene proportions in stem resin and shoot emissions within one tree were not identical and the tree-to-tree variation in the shoot emissions was larger than in the resin composition. In resin, the proportions of Δ^3-carene and α-pinene varied generally only slightly between trees, whereas the shoot emissions of certain trees were clearly dominated by either of the compounds (Figure 10). Moreover, α-pinene was generally more abundant in shoot emissions than in the resin, probably because of its high volatility compared to the other monoterpenes. Interestingly, the proportions of β-pinene were only considerable in two trees, but it proved an important component of both the shoot monoterpene emissions and stem resin of these trees (Figure 10).

Mismatches between the stem resin composition and shoot emission spectrum may be expected (Vanhatalo et al. 2018): in addition to emission from storages, the shoots directly emit monoterpenes upon synthesis (Ghirardo et al. 2010; Harley et al. 2014), the different monoterpenes have different volatilities and diffusion rates, and the resin composition may differ between the stem and shoots (Latta et al. 2000). The resin composition difference between the stem and shoots may strongly affect the emission patterns between these two tree parts according to data collected in the Pfynwald forest: comparing the monoterpene emissions and resin composition within the same tree part, stem or shoot showed better matches (unpublished data).

Resin pressures also varied between trees. In general, trees with higher resin pressure had higher monoterpene contents in their resin, especially of α-pinene, and larger monoterpene emissions, especially Δ^3-carene and terpinolene from their shoots. These connections between resin pressure, resin composition and monoterpene emissions may reflect past stress events that have increased resin pressures and the production and emissions of certain monoterpenes.

4.2.2 Resin pressure and water availability effects on monoterpene emissions from the stem

Study I showed that like the resin pressure dynamics, the daily monoterpene emission dynamics from a Scots pine stem followed temperature (Figure 11). We used the EFRA analysis to separate the potential effects of temperature and resin pressure on the monoterpene emissions (Figure 7). The analysis indicated that both temperature and resin pressure were important in explaining the monoterpene emissions. Temperature affects the monoterpene emissions by regulating their vapour pressures and diffusion rates, and resin pressure may increase monoterpene emissions by facilitating their release from the resin ducts and stem. According to EFRA, a portion of the temperature effect on monoterpene emissions may be mediated through the temperature effect on resin pressure, but resin pressure also had an independent impact. The independent resin pressure impact could be connected to subtle short-term changes and larger long-term changes in resin pressure, caused by slow changes in water availability and water potential in the xylem.

Correspondingly, the daily mean stem monoterpene emission potential, normalised for the short-term effects of temperature, correlated with daily mean soil water content and xylem water potential (study III) (Figure 11). Anomalies of high monoterpene emission potential occurred when soil water content and xylem water potential were higher than average. This effect probably manifests the long-term variation in resin pressure, but at least a part of it may also result from more direct effects of humidity on monoterpene emissions. Abundant

water availability may enhance monoterpene production, and air humidity may provoke monoterpene release from short-term storages or resin ducts as a result of the uneven wetting and swelling of stem tissues, as suggested by Staudt et al. (2019), or because of the changes in bark conductance, as proposed for leaf cuticula (Croteau et al. 1977).

Completely separating the effects of temperature and resin pressure on stem monoterpene emissions is impossible in the moist conditions of Hyytiälä because temperature and resin pressure covary. Thus, it would be interesting to study the connections between resin pressure and stem monoterpene emissions in conditions where resin pressure dynamics diverge from temperature dynamics. This may be achieved in a dry environment, where resin pressure is regulated by water potential more than temperature.

Another interesting question concerns the effect of resin pressure on monoterpene emissions from pine shoots. Resin pressures or pressure variations within pine needles are not known, but if they follow the same dynamics as in the stem, a part of the temperature effect on shoot monoterpene emissions may also be explained by resin pressure. The effect of resin pressure may also partly explain the decrease in monoterpene emissions during drought (Staudt et al. 2002; Lüpke et al. 2016). However, these suggestions remain hypothetical until resin pressures are measurable within the resin ducts of needles.

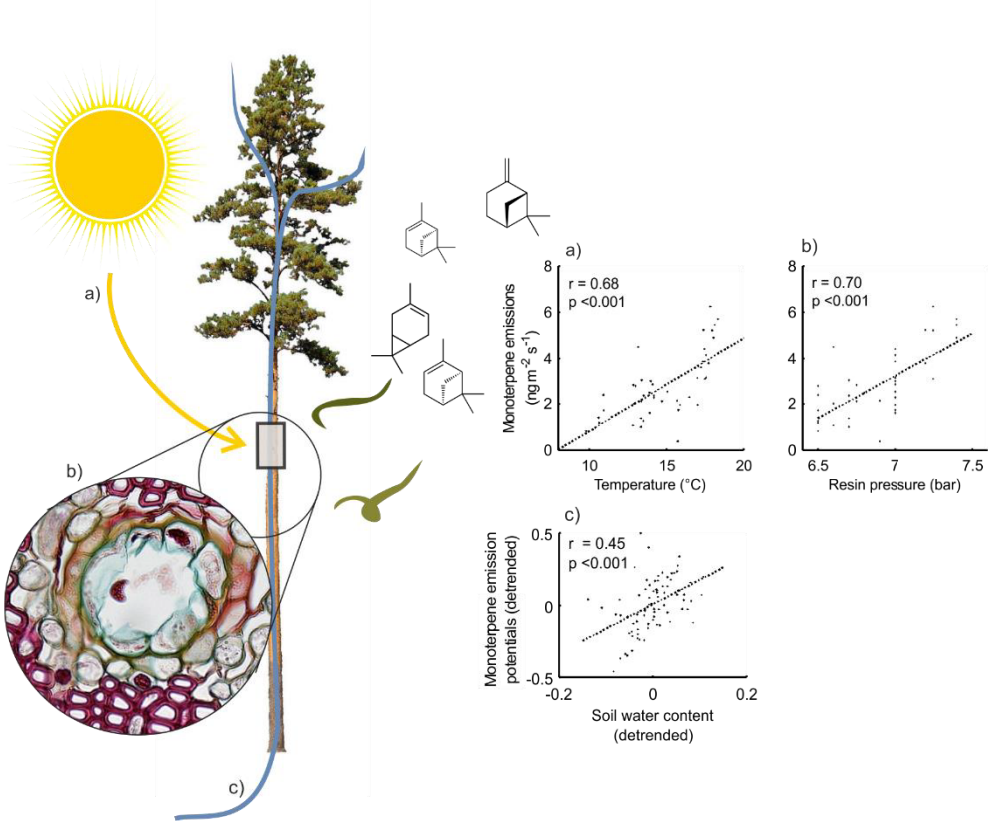

Figure 11. Monoterpene emissions from a Scots pine (*Pinus sylvestris*) stem explained with a) temperature and b) resin pressure, 15.-18.7.2013 (study I) and c) soil water content in June-August 2015 (study III), in Hyytiälä, Finland.

4.3 Water transport effects on OVOC emissions

4.3.1 OVOC emissions from the shoots

Like most VOC emissions, the shoot emissions of water-soluble oxygenated VOCs (OVOCs) – methanol, acetone and acetaldehyde – depend on temperature. They are also considered dependent on stomatal conductance, methanol in particular, and acetone and acetaldehyde to a lower degree. When stomatal conductance is small, the capacity of these compounds to dissolve in water inhibits the increase of their concentration within the leaf air space, which may cause a momentary reduction in their emissions (Niinemets and Reichstein 2003).

Nevertheless, study IV showed that transpiration rather than stomatal conductance controlled the shoot OVOC emissions from Scots pine in field conditions. The emissions were best explained by temperature and transpiration, and according to the structural equation model, stomatal conductance affected the emissions only indirectly by regulating transpiration. The strong coupling of OVOC emissions with transpiration suggests that a part of the OVOCs measured from the shoots evaporate from transpired xylem sap (Figure 12). It also indicates that these OVOCs or their precursors may be transported within the xylem sap from their sources in the roots and stem up to the shoots and ambient air, as suggested in the case of methanol (Grabmer et al. 2006; Folkers et al. 2008) and acetaldehyde (Kreuzwieser et al. 2000; Fall 2003).

Due to the transport, a certain proportion of OVOC shoot emissions may originate from the stem or roots. How large this transported proportion is compared to the proportion that originates from the shoot depends on 1) how much of these compounds are produced in the shoots versus the stem and roots and 2) where in the stem or roots they are mainly produced. Methanol is produced in the growing tissue of the stem and roots, near the stem surface, so it may more likely diffuse through the bark to the ambient air rather than dissolving into the xylem sap. Thus, the proportion of transported methanol of the total shoot emissions is probably small. In contrast, acetaldehyde mainly originates from the roots and the anoxic parts of the stem, so it may more likely dissolve in xylem sap rather than diffuse through sapwood and bark to the ambient air. Thus, the proportion of transported acetaldehyde of the total shoot emissions is probably larger. In line with this hypothesis, stem OVOC emissions were dominated by methanol, although the methanol emissions from the shoots were slightly smaller than the shoot emissions of acetone and acetaldehyde (study IV). Furthermore, the shoot emissions of methanol were generally better explained by temperature than by transpiration rate, indicating a larger proportion of locally produced methanol. The shoot emissions of acetone and acetaldehyde in particular were generally better explained by transpiration rate than temperature, indicating an important role of the transported portion.

4.3.2 OVOC emissions from the stem

The daily emissions of methanol and acetaldehyde from Scots pine stems were also temperature-dependent, but like their emission patterns from the shoots, the stem emission patterns reflected the effect of transport in the xylem sap (study III). The increased acetaldehyde emission potential occurred after anomalies of high soil water content, with a lag of a couple of days (Figure 12). The lag times corresponded to the average xylem sap transport times, calculated from the average transpiration rates, from the base of the stem to the measurement location at the top of the stem (Figure 12). The lagged effect of soil water content indicates that acetaldehyde production in the soil and roots follows water availability even when the soil is not flooded or anoxic and that the transport in the xylem sap also affects

acetaldehyde emissions from the stem. In addition to the transported acetaldehyde, some stem acetaldehyde emissions may originate from lack of (O_2) near the heartwood or in the cambium during rapid stem growth that may cause the formation of ethanol and acetaldehyde (Kimmerer and Stringer 1988). This local production may explain the correlations found between stem acetaldehyde emissions and stem growth along with stem CO_2 efflux (Study III), but its significance to total acetaldehyde emissions is unknown.

A weaker effect of soil water content was found on the methanol emission potential (Figure 12). The fact that the effect of soil water content was smaller highlights the complexity of methanol sources in the stem: a large portion of the methanol measured from the stem probably originates from the local production connected to stem growth, whereas another part may be transported from the roots and the lower parts of the stem. In addition, a part of the local production may dissolve in the xylem sap or be metabolised (Jardine et al. 2017). To describe the methanol emissions more accurately, the sources and sinks would need to be separated and the lag times between growth, methanol production and emissions estimated. The methanol emissions potential from the stem also correlated with bark water conductance, indicating that the diffusion through bark may be an important constraint for the emissions.

Acetone emissions from the stem followed temperature changes poorly and the emission dynamics were generally related to air humidity. Further studies are necessary for first locating the main acetone sources in trees and then for understanding its emission patterns from the stem. Transport in the xylem sap may play an important role, as the emission patters from shoots closely followed transpiration.

The spatial pattern of OVOC emissions from various stem heights corresponded to the stem CO_2 efflux pattern that is also affected by transport in the xylem sap (study IV) (Hölttä and Kolari 2009). Emissions were low in the bottom part of the stem, where diffusion to ambient air is slow due to the thick bark and the compounds easily dissolve in the xylem sap. Emissions were higher in the middle part of the stem and highest in the top. At the top, diffusion is rapid through the thin bark, and the xylem sap may already have had high OVOC concentrations, enhancing their release. The top part of the stem is also more active (Vanhatalo 2018) and more exposed to changes in temperature, contributing to higher emissions.

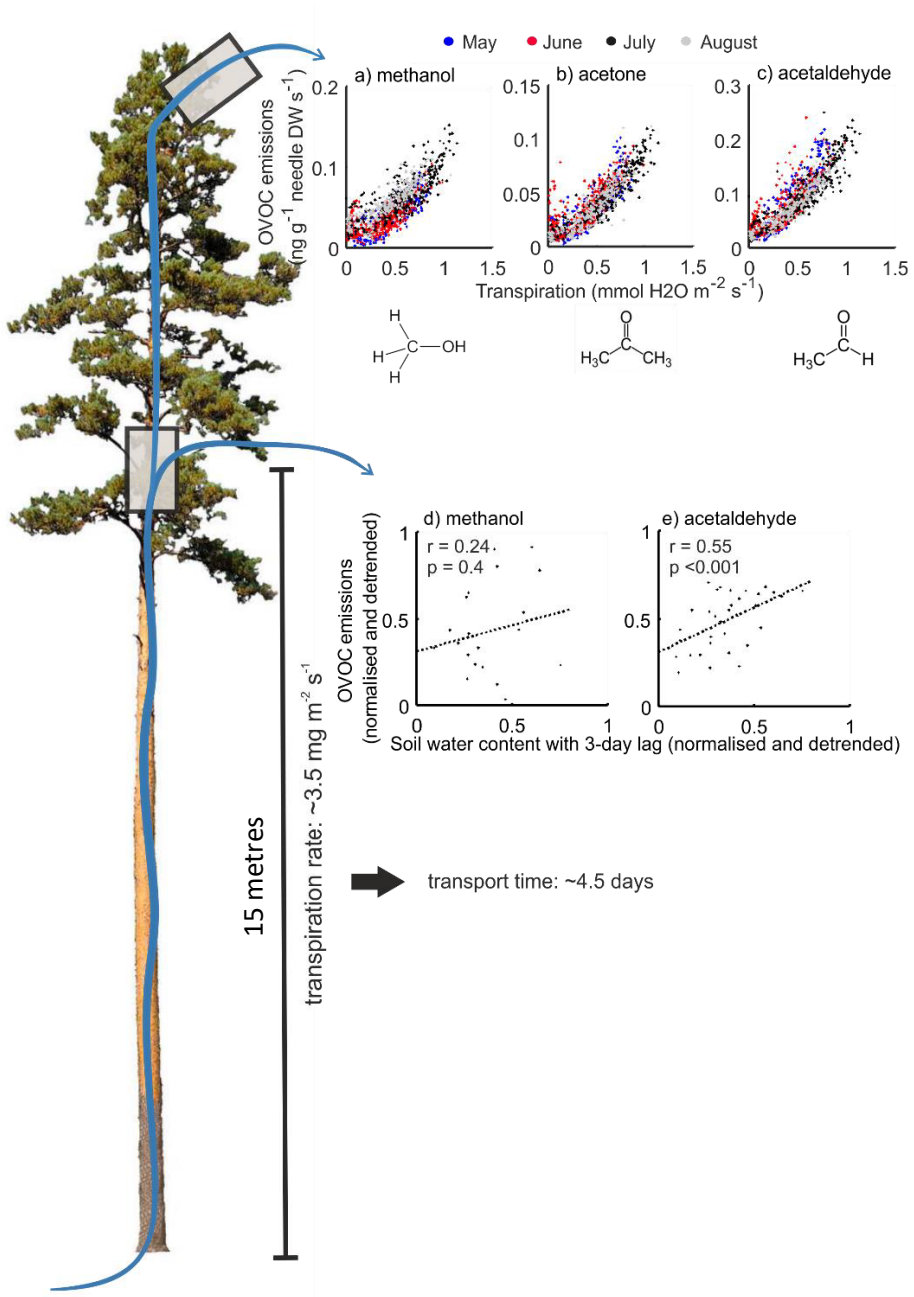

Figure 12. The framework of soil water and xylem sap transport on OVOC emissions (methanol, acetone and acetaldehyde) from a Scots pine (*Pinus sylvestris*) shoots and stem. Effects of transpiration on shoot emissions of a) methanol, b) acetaldehyde and c) acetone in Hyytiälä, 2010. No lags were detected in the effect of transpiration on shoot OVOC emission. Effect of soil water content with a 3-day lag on stem emissions of d) methanol and e) acetaldehyde in Hyytiälä, 2017. The lag time of 3 days is in the same scale as the roughly estimated transport time of water from the tree base to the measurement location at 15 metres calculated based on the average summertime transpiration rate.

5 CONCLUSIONS

In contrast to a dry environment, Scots pine resin pressure in a moist environment is controlled by temperature in the short term, most likely because of thermal expansion and the temperature-dependent changes in solubility of gases in resin. In the longer term, the direct temperature effect is less important or even negative, and resin pressure is affected by changes in water availability and tree water status. This impact of water status suggests that even in a moist environment, the defence capacity of Scots pine may be reduced during drought periods because of decreasing resin pressures.

In addition to tree defence, resin pressure along with temperature also affect the monoterpene emissions from a Scots pine stem. A part of the resin pressure effect seems to be caused by temperature, but it also has an independent effect on the emissions that is probably linked to the long-term trends of water availability and water potential in the xylem. For example, a high stem monoterpene emission potential may be observed when soil water content is higher than average. In addition to temporal variation, resin pressure and composition are associated with the tree-to-tree variation of monoterpene emissions. On the one hand, monoterpenes stored in the resin may be emitted from the stem and foliage, contributing to the spectrum and quantity of monoterpenes emitted from the tree. However, in foliage, the *de novo* emissions of monoterpenes cause some diversion of the emission spectrum from the resin composition. On the other hand, a tree with high resin pressure may have larger monoterpene emissions from the shoots. Thus, knowledge on resin dynamics and variability play an important role in advancing the understanding of the tree-to-tree variation and tree-level monoterpene emissions of conifers.

Apart from monoterpenes, conifer trees are large sources of OVOCs: methanol, acetone and acetaldehyde. Their emissions from Scots pine are not dependent on resin but are also strongly regulated by temperature and tree water relations owing to their water solubility. Upon production, these compounds may dissolve in the xylem sap and travel from their sources in the soil, roots and stem up to the foliage. Thus, a part of the OVOCs emitted from the foliage originates from other tree parts and the OVOC emissions from the foliage are strongly dependent on transpiration. Transpiration and soil water content also affect the stem emissions of acetaldehyde and, to a smaller degree, of methanol. Their emission potential from the stem increase after anomalies of high soil water content with a lag that corresponds to their transport time in the xylem sap.

The results of this thesis highlight the strong impact of temperature on all the studied tree processes in a boreal environment that has moderate or minor limitations in water availability. However, while temperature may be used to predict resin pressure and VOC emissions from the stem and foliage at a short time scale, the interconnection between tree water relations and resin and VOC emissions dynamics may cause unpredicted dynamics at a longer time scale and especially in the case of extreme events such as drought or flooding.

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